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(71) Applicant: THE UNIVERSITY OF FLORIDA [US/US]; Gainesville, FL 32611 (US).

(72) Inventors: SINGH, Rajiv, K.; 8615 SW 19th Road, Gainesville, FL 32605 (US). FITZGERALD, James; 4101 Northwest 21st Terrace, Gainesville, FL 32605 (US).

(74) Agent: SAITTA, Thomas, C.; Law Office of Thomas C. Saitta, P.A., Suite 203, 6821 Southpoint Drive North, Jacksonville, FL 32216 (US).

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(54) Title: PROCESS FOR DEPOSITING ATOMIC TO NANOMETER PARTICLE COATINGS ON HOST PARTICLES

(57) Abstract

A method of coating a plurality of host particles ranging from several nanometers to several millimeters in diameter with coating particles sized from atomic size to 10 nanometers produced by physical vapor deposition, preferably laser ablation, where said host particles are coated either discontinuously or continuously by positioning them in the ablation flux and fluidizing or agitating the host particles to prevent agglomeration during the coating step, and the coated host particles themselves.

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PROCESS FOR DEPOSITING ATOMIC TO NANOMETER PARTICLE COATINGS ON HOST PARTICLES

BACKGROUND OF THE INVENTION

This invention relates in general to the field of coating a substrate where physical vapor deposition (PVD) techniques for creating extremely small or atomic size species in a flux, such as laser ablation, thermal evaporation or sputtering, are used to deposit coating material onto the substrate. More particularly, the invention relates to the field of material coating where the substrate consists of individual host particles rather than a film or bulk substrate. Even more particularly, the invention relates to depositing a number of discrete particles on the host particles to form generally uniform discontinuous or continuous coatings on the individual host particles, where the coating particles vary in size from atomic to nanometer scale particles.

A well known technique for coating a bulk or thin film substrate with a separate material, known as physical vapor deposition (PVD), is to provide a target object composed of the coating material in relatively close proximity and parallel to the substrate surface, then striking the target with an energy beam to free discrete particles of the coating material from the target, the discrete particles then adhering to the substrate. In the PVD method known as laser ablation, a laser is used to supply the energy to create the coating particles. Laser ablation works well with multicompositional coatings where the composition of the targets are directly transferred onto the substrate. While this technique is very successful for providing continuous thin film coatings on bulk substrates, it is not readily applicable for substrates consisting of discrete host particles, and is

especially not applicable for applying uniform discontinuous coatings where the size of coating particles is to be in the range of atomic size to only a few nanometers. If not properly controlled, the coating particles produced by laser ablation may agglomerate prior to adhesion to the host particles to form coating particles of greater than desired size. As the aggregation strength of the agglomerated coating particles is expected to be very high, the usefulness of these particles as coatings on the host particles is significantly reduced. Additionally, this and other coating techniques often result in the individual host particles agglomerating into a unified mass.

There are many applications where discontinuous or continuous nano-particle or smaller size coatings on host particulates are desirable, such as in flat panel displays, sintering of advanced ceramics and in rechargeable batteries. The nano-particle coatings on the host particles can increase surface area, produce higher catalytic activity, increase adhesion and lower sintering temperatures. Surface properties of the host particles relating to heat transfer, electrical, adsorption, desorption, and reflectivity can be altered. Through the methodology of the invention, it has been found that the size of the coating particles and the coating parameters can be controlled such that a number of individual host particles can have a controlled number or amount of discrete coating particles, sized from atomic size to a few nanometers, adhered in a well dispersed pattern onto the surface of the host particles.

It is an object of this invention to provide discrete, relatively large, host particles with a discontinuous or continuous surface coating of discrete particles, sized as small as a few nanometers down to atomic scale, through a PVD method such as laser ablation method. It is a further object to provide such coated particles by a method where the

cluster size of the individual coating particles and the amount of surface coverage of the individual coating particles can be controlled to prevent agglomeration of the individual coating particles. It is a further object to provide means to prevent the coated host particles from agglomerating.

SUMMARY OF THE INVENTION

Host particles, which may range in size for example from several nanometers to several millimeters in diameter, are provided with a relatively uniformly dispersed discontinuous or continuous coating of discrete individual coating particles sized from atomic scale to a few nanometers. The coating particles are created by a PVD process, and preferably by laser ablation, where a pulsed laser beam is aimed at a target composed of the coating material under conditions sufficient to release individual particles from the target in a generally perpendicular ablation flux. The laser ablation technique is especially suited for multi-elemental deposition in which the stoichiometry of the ablated species is maintained. The size of the coating particles can be varied from atomic species to nanometer species by controlling the gas pressure in the system. The chamber pressure can be dynamically varied with time to control the agglomeration zones. During laser ablation, the host particles are kept agitated or fluidized such that there is continual relative movement between all the host particles. The fluidization of the host particles can be accomplished by various means, such as mechanical vibration or impaction of a container designed to provide exposure of the host particles to the coating particles. The

degree of coating is controlled by varying the laser parameters, energy density and number of pulses, gas pressure within the treatment chamber, and the treatment time.

DETAILED DESCRIPTION OF THE INVENTION

The invention in general comprises a method or process, and the articles produced by this method, for creating host or core particles with discrete particles adhered generally uniformly to the surface of the host particles to form continuous or discontinuous coatings where the individual host particles remain non-agglomerated after the deposition step. The coating particles are extremely small, being sized from atomic to a few nanometers in diameter, relative to the host particles, which are sized from several nanometers to several millimeters in diameter. The method utilizes physical vapor deposition (PVD) such as thermal evaporation, sputtering, or preferably laser ablation of a target material to produce a flux of coating particles, and fluidization means to agitate the host particles during the coating process to prevent agglomeration.

Laser ablation of a target material to produce free particles of the target material which adhere to a substrate is a well known technique. A sealable chamber is provided so that the atmosphere within the chamber may be controlled as to the particular gases present and as to the partial pressure within the system using common technology. A target composed of the desired coating material is mounted, preferably rotatably, within the chamber and a UV transparent quartz window is provided through which a laser beam can be directed to strike the target. A typical laser which has been used experimentally

for the methodology of this application is a Lambda Physik model 305i pulsed excimer gas laser with an operating wavelength of 248 nanometers. Many other suitable lasers may be substituted therefore. The laser beam will produce a particle flux generally perpendicular to the surface of the target. Laser ablation is preferred since under optimized conditions the removal of species from the target takes place in a stoichiometric manner. Other well known PVD techniques which produce atomic to nanometer scale ablated species in a flux, such as thermal evaporation and sputtering, may also be utilized.

The host or core particles are generally large relative to the size of the coating particles, with the method proven to be very applicable to host particles sized from 0.5 to 100 microns. It is understood that the host particles can be smaller, down to several nanometers in diameter, or larger, up to several millimeters in diameter, than this range if so desired. The host particles are retained within a processing container which has a large enough volume to permit movement of the particles within the container. The top of the container is open and the container maintained in a vertical position during fluidization, or a portion of the processing container, such as a part or all of a side or bottom, is provided with openings or apertures to retain the host particles within the processing container, if the particle deposition is to occur laterally or from below. A suitable construction for the processing container has been found to be a cylindrical glass vial with one open end; the open end being covered, if necessary, by a wire mesh or screen with apertures slightly smaller than the size of the host particles. The processing container is mounted within the treatment chamber with the open end facing the target at a distance of from approximately 3 to 10 centimeters such that the majority of particles in the perpendicular flux from the target will enter the processing container and contact

the host particles. The system may also be constructed with continuous or incremental transport means for the host particles, such as a conveyor system, whereby the host particles can be moved relative to the ablation flux during the coating process so that coating may occur in a continuous manner.

The host particles must be agitated or fluidized in some manner to expose the entire surface of each host particle to the coating particles entering the processing container to insure general uniformity of coating and to assist in the prevention of agglomeration of individual host particles. This fluidization may be accomplished in a number of equivalent manners, such as by mechanical agitation by vibration, rotation or movement of the processing container, by providing a stirring device within the container, or by pneumatic agitation by passing gas flow through the host particles. Another means to accomplish the required fluidization is to intermix magnetic particles, such as iron, with the host particles and then to apply an alternating magnetic field to the processing container during the deposition of the coating particles. The magnetic particles are separated from the host particles after the treatment process.

The percentage of deposition or coverage of the coating particles on the host particles is controlled by controlling the size of the coating particles and the treatment time. The longer the treatment time, the more coating particles will be adhered to the surface of the host particles, increasing both the percentage of coverage and the thickness of the coating layer. Surface coverage can be adjusted from below 1 percent up to 100 percent. The size of the coating particles is controlled by the atmospheric composition and partial pressure within the treatment chamber. By dynamically controlling the gas pressure the reaction zone for forming the coating particles can be controlled. Reactive

gases such as oxygen, ammonia or nitrous oxide produce higher concentrations of molecular, as opposed to atomic, species within the ablated particle flux, and are used if deposition of oxide, nitride or similar particles is desired. Pressure within the chamber determines the number of collisions between ablated coating particles, with higher pressure causing more collisions and therefore larger coating particles in the ablated flux. Pressure within the system may vary greatly, from 10^{-6} to 10 Torr for example, but production of 1 to 10 nanometer or smaller coating particles typically occurs at approximately 400 mTorr or higher, and production of atomic particles occurs at below approximately 300 mTorr.

EXAMPLE 1

Atomic scale titanium dioxide coating particles were deposited onto silicon dioxide host particles under the following conditions: laser focal lens at 7.5 cm, laser pulse rate at 35 hz for 8 minutes at 600 mJ and energy density of 3 to 6 J/cm^2, argon atmosphere, 120 mTorr starting partial pressure and 180 mTorr ending partial pressure. The host particles were retained in a cylindrical glass vial approximately 1 inch in diameter and 2 inches in length with an open end covered by a wire mesh. The host particles were agitated using magnetic stirring. SEM (scanning electron microscope) photomicrography of the host particles and wavelength dispersive x-ray maps of the titanium on the surface of the host particles show a generally uniform but discontinuous deposition of discrete particles of titanium dioxide.

EXAMPLE 2

Nano-scale silver coating particles were deposited onto silica host particles under the following conditions: laser focal lens at 7.5 cm, laser pulse rate at 30 hz for 9 minutes at 450 mJ and energy density of 3 to 6 J/cm^2. 17 mTorr starting partial pressure and 10 mTorr ending partial pressure. The host particles were retained in a cylindrical glass vial approximately 1 inch in diameter and 2 inches in length with an open end covered by a wire mesh. The host particles were agitated using magnetic stirring. SEM photomicrography of the host particles and wavelength dispersive x-ray maps of the silver on the surface on the silica host particles show a generally uniform but discontinuous deposition of discrete particles of silver.

EXAMPLE 3

Nano-scale silver coating particles were deposited onto silica host particles under the following conditions: laser focal lens at 7.5 cm, laser pulse rate at 15 hz for 40 minutes at 450 mJ and energy density of 3 to 6 J/cm^2. 19 mTorr starting partial pressure and 21 mTorr ending partial pressure. The host particles were retained in a cylindrical glass vial approximately 1 inch in diameter and 2 inches in length with an open end covered by a wire mesh. The host particles were agitated using magnetic stirring. SEM photomicrography of the host particles and wavelength dispersive x-ray maps of the silver on the surface on the silica host particles. showing a generally uniform but discontinuous deposition of discrete particles of silver.

It is understood that equivalents and substitutions for elements set forth above may be obvious to those skilled in the art, and therefore the true scope and definition of the invention is to be as set forth in the following claims.

We claim:

1. A method for uniformly coating individual host particles with coating particles formed using a physical vapor deposition technique and capable of adhering to said host particles, comprising the steps of providing a number of host particles, providing a target composed of a material selected from the group of materials able to be formed into coating particles using a physical vapor deposition technique and which adhere to said host particles, creating a flux of coating particles smaller than said host particles from said target using a physical vapor deposition technique, coating said host particles with said coating particles by positioning said host particles in said flux, and fluidizing said host particles to provide relative movement of said host particles during said coating step to prevent agglomeration and non-uniformity of coating of said host particles.

2. The method of claim 1, further comprising controlling said particle creating step such that said coating particles are smaller than about 10 nanometers.

3. The method of claim 2, further comprising providing said host particles with diameters in the range of about two nanometers to about two millimeters in diameter.

4. The method of claim 1, further comprising controlling the time length of said coating step such that said coating step produces a discontinuous coating on said host particles.

5. The method of claim 1, further comprising controlling the time length of said coating step such that said coating step produces a continuous coating on said host particles.

6. The method of claim 1, where said fluidization of said host particles is performed by mechanically vibrating a container of said host particles.

7. The method of claim 1, where said fluidization of said host particles is performed by impacting a container of said host particles.

8. The method of claim 1, where said fluidization of said host particles is performed pneumatically.

9. The method of claim 1. where said fluidization of said host particles is performed by magnetic stirring.

10. The method of claim 1, where said host particles are continuously positioned in said flux.

11. The method of claim 1. where said particle creating step is performed by laser ablation.

12. The method of claim 11. where said laser ablation is performed at pressures from 10^{-6} to 10 Torr.

13. The method of claim 11, where said laser ablation is performed at pressures less than 300 mTorr.

14. A coated host particle having a diameter in the range of about two nanometers to about two millimeters, said host particle being surface coated with coating particles produced by physical vapor deposition. said coating particles having a size smaller than 10 nanometers.

15. The host particle of claim 14, where said coating particles form a discontinuous coating on the surface of said host particle.

16. The host particle of claim 14. where said coating particles form a continuous coating on the surface of said host particle.

17. A plurality of coated host particles having diameters from about two nanometers to about two microns and coated surfaces comprising adhered coating particles, said coated host particles produced by creating a flux of coating particles having a size smaller than about 10 nanometers using physical vapor deposition. coating said host particles with said coating particles by positioning said host particles in said flux, and fluidizing said

host particles during said coating step to insure general uniformity of coating and to prevent agglomeration of said host particles.

18. The coated host particles of claim 17, where said coating is discontinuous.

19. The coated host particles of claim 17, where said coating is continuous.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/05431

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C23C 14/22, 14/34; B23B 5/16
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/596, 597, 212, 213, 215, 216, 217, 219, 220, 222, 248.1, 255.5 184, 185; 204/192.1, 192.15; 428/403, 404, 405, 406, 407

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, STN

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US 4,046,712 A (CAIRNS et al.) 06 September 1977, col. 2, lines 25-55; col. 7, lines 18-45.	1-7, 10, 14-19 — 8-9, 11-13
X — Y	US 4,940,523 A (TAKESHIMA) 10 July 1990, col. 3, lines 30-65; col. 5, lines 40-68.	1-5, 10, 14-19 — 6-9
X — Y	US 5,489,449 A (UMEYA et al.) 06 February 1996, col. 2, lines 25-68; col. 3, lines 5-30.	1-5, 8, 10, 14-19 — 6-7, 9, 11-13

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	LUNNEY, JAMES G., Pulsed Laser Deposition of metal and Metal Multilayer Films, Applied Surface Science, 1995, Vol. 86, pp 79-85, especially pages 79-80.	11-13

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

427/596, 597, 212, 213, 215, 216, 217, 219, 220, 222, 248.1, 255.5 184, 185; 204/192.1, 192.15; 428/403, 404, 405, 406, 407

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